Kinetics of the Cycloadditions of Diphenylketene with 1,1-Diarylethylenes and Styrenes[1]

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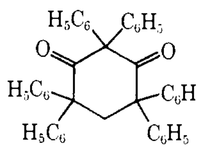
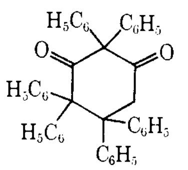
Abstract: The cycloadditions of diphenylketene with 1,1-diarylethylenes and 4-substituted styrenes at 119.96° in bromobenzene give linear Hammett plots: for the diarylethylenes, $\log k_{rel} = -0.78(2\sigma)$, while $\log k_{rel} = -0.73\sigma$ for the styrenes. The 2,2-diphenyl-3,3-diarylcyclobutanones formed in the rate-determining step of the first cycloadditions react further with diphenylketene to produce 2:1 adducts, previously and incorrectly formulated as cyclohexane-1,3-dione derivatives. The styrene–diphenylketene adducts, 2,2-diphenyl-3-arylcyclobutanes, are stable under the reaction conditions. 1,1-Diphenylethylene reacts with diphenylketene 62 times slower than styrene. The styrene–diphenylketene reaction shows only a minute rate dependence on solvent polarity in bromobenzene, *o*-dichlorobenzene, di(β-chloroethyl) ether, and dimethylformamide. These data are interpreted as evidence supporting a concerted mechanism for both reactions leading to 2,2,3-triphenyl- and 2,2,3,3-tetraphenylcyclobutanones.

Diphenylketene and 1,1-diphenylethylene give a 2:1 adduct $C_{42}H_{32}O_2$, mp 182°, for which Staudinger and Suter assigned structure **1**.[4] Farooq and Abraham[5] found the adduct when heated with methanolic sodium hydroxide gave equimolar amounts of diphenylacetic acid and a β-hydroxy ketone, 1,1,4,4-tetraphenyl-4-hydroxy-2-butanone; they proposed structure **2** for the adduct and suggested its formation by way of the dipolar intermediate **3**.



1



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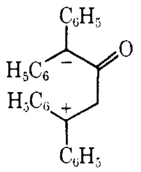


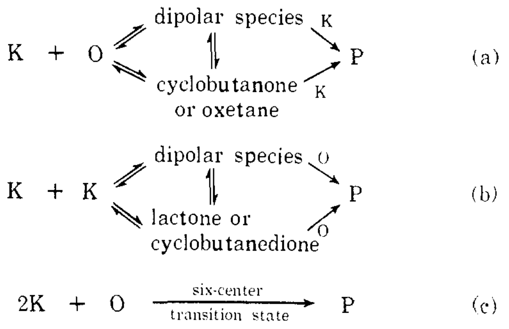
3

The steric crowding expected from four phenyl groups on two adjacent carbon atoms in a cyclobutane ring was considered adequate rationale for the formation of a six- rather than a four-membered ring adduct, the type of product obtained from cycloadditions of diphenylketene with styrenes.

In an effort to clarify the diphenylketene–1,1-diphenylethylene reaction, especially with regard to the possible intermediacy of dipolar intermediate **3**,[6] a thorough kinetic investigation of this and closely related systems was undertaken.

The two-step dipolar mechanism and a variety of other possibilities are included in the three kinetic mechanisms outlined in Scheme I; these possibilities were quickly restricted by fresh experimental data.

Scheme I. Mechanistic Alternatives for the Addition of Diphenylketene to 1,1-Diphenylethylene[a]



[a] O = olefin, K = diphenylketene, P = product.

Results and Discussion

The kinetics of the reaction of diphenylketene and 1,1-diphenylethylene were studied by nmr spectroscopy in bromobenzene solution at 119.96° (±0.02°). A reaction mixture containing the ketene, olefin, solvent, and hexamethylbenzene as a standard for integration was degassed and sealed under vacuum in an nmr tube. The initial ratio of olefin to internal standard was determined by integration of the corresponding nmr peaks. The sample was heated at 119.96° for measured intervals, quenched in ice water, analyzed by nmr, and returned to the kinetic bath for further reaction.

The data were analyzed in terms of first, second, and third-order differential rate equations.

$$d[P]/dt = k_1[O]$$

$$d[P]/dt = k_2[O][K]$$

$$d[P]/dt = k_3[O][K]^2$$

The integrated forms of these rate equations[7] and a conventional, unweighted linear squares treatment[8]

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[3] National Science Foundation Predoctoral Trainee, 1965–1968.

[4] H. Staudinger and E. Suter, *Ber.*, **53**, 1092 (1920).

[5] M. O. Farooq and N. A. Abraham, *Bull. Soc. Chim. Fr.*, 832 (1958).

[6] See R. Gompper [*Angew. Chem. Intern. Ed. Engl.*, **8**, 312 (1969)] for a timely review of polar intermediates in cycloadditions.

[7] S. W. Benson, "Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, Chapter II.

[8] (a) W. C. Hamilton, "Statistics in Physical Science," Ronald Press, New York, N. Y., 1964; (b) "FORTRAN in the Physical Sciences," IBM, Technical Publications Department, White Plains, N. Y., 1965.

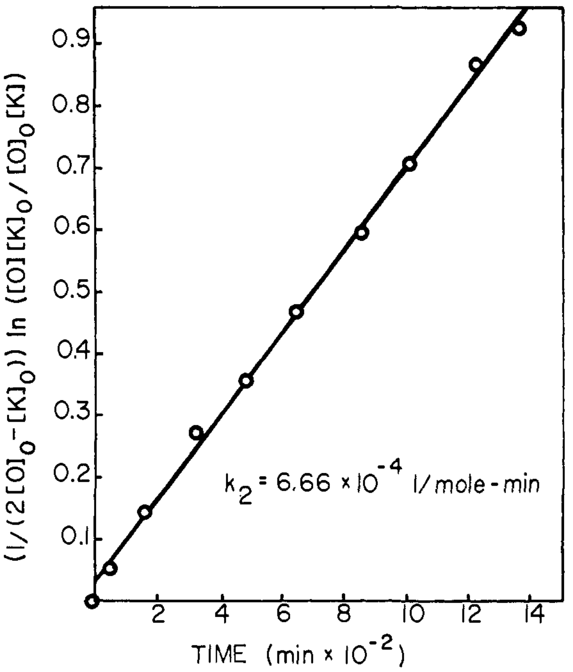

Figure 1. Typical kinetic plot for the reaction of diphenylketene with 1,1-diphenylethylene at 119.96° in bromobenzene.

were employed to obtain the best fit to the kinetic data. Computations were carried out using an IBM 1800 computer.

The rate-determining step of the reaction was found to be first order in diphenylketene and first order in diphenylethylene. This fact eliminates from mechanistic consideration Schemes Ib and Ic which would require kinetics second order in ketene alone or third order overall. The results also point to the first step in Scheme Ia as the rate-determining one. A second-order kinetic plot for a typical run is given in Figure 1. The first point was neglected in calculations giving k_2 when it exceeded twice the average standard deviations of the remaining points. Reactions were taken to approximately 70% completion before the nmr method became impractical. No corrections for concentration changes between room temperature and the reaction temperature were made.

The rate-determining first step in Scheme Ia might lead to a dipolar intermediate such as **3** or to a neutral, relatively unstable substituted oxetane or cyclobutanone. One useful approach toward making this distinction would be to investigate the effect of aryl substituents upon reaction rate. Rate-determining formation of a dipolar intermediate would be expected to display a sensitive correspondence between reaction rate and the electronic characteristics of substituents. Aryl substitution in the olefin would be expected to generate rates correlating with a negative value of the Hammett reaction constant ρ; the magnitude of ρ would depend upon the degree of polar character in the transition state.[9]

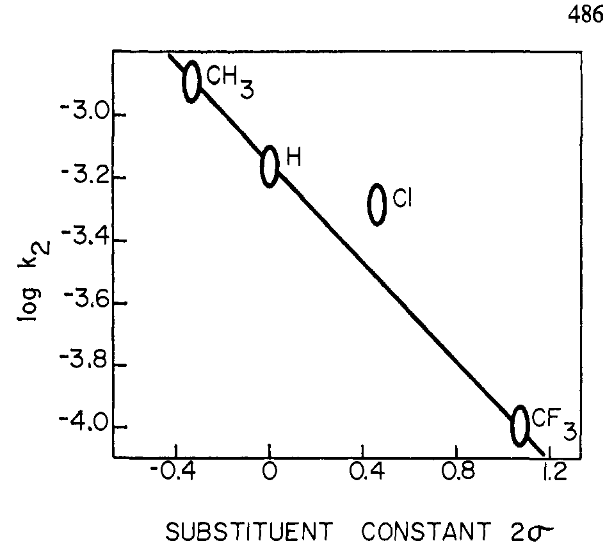

Figure 2. Plot of log k_2 against 2σ for the reaction of diphenylketene with 1,1-diarylethylenes at 119.96° in bromobenzene.

The diarylethylenes with the exception of 1,1-bis(*p*-trifluoromethylphenyl)ethylene were prepared by treatment of the correspondingly substituted benzophenones with methylmagnesium iodide followed by dehydration of the resulting tertiary alcohol. The *p*-methoxy-substituted alcohol underwent spontaneous dehydration on acidic work-up; others required heating to effect loss of water. The olefin 1,1-bis(*p*-trifluoromethylphenyl)ethylene, which has not been reported in the literature, was prepared from ethyl acetate and *p*-trifluoromethylphenylmagnesium bromide, followed by acidic dehydration. The olefin, a low-melting waxy solid, was characterized by its spectral properties.

The kinetic runs were carried out in bromobenzene at 119.96° in a manner similar to that employed for the unsubstituted olefin. For the reaction involving the methyl-substituted olefin, *p*-di-*t*-butylbenzene was used as the internal standard. The very low solubility of the *p*-methoxy-substituted olefin made it unsuited for the kinetic work, but the adduct itself was prepared and characterized. When diphenylketene was added to a solution of 1,1-bis(*p*-methylaminophenyl)ethylene, a dark viscous mixture was formed which resulted in line broadening in the nmr. Because of the line broadening and possible kinetic complications resulting from complex formation, this olefin was not considered further.

The results of the kinetic runs for 1,1-diarylethylenes are given in Table I. Figure 2 is a plot of the log

Table I. Rate Constants for the Addition of Diphenylketene with 1,1-Diarylethylenes in Bromobenzene at 119.96°

X in (p-XC$_6$H$_4$)$_2$C=CH$_2$	2σ	$k \times 10^4$, l./mol min
CF$_3$	1.08	1.00 ± 0.06
Cl	0.46	5.18 ± 0.39
H	0	6.76 ± 0.19
CH$_3$	−0.34	12.7 ± 0.73

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(9) For reviews, (a) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953); (b) P. R. Wells, *Chem. Rev.*, **63**, 171 (1963); (c) S. Ehrenson in "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitweiser, and R. W. Taft, Ed., John Wiley & Sons, Inc., New York, N. Y., 1964, p 195; (d) C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry," Vol. 2, John Wiley & Sons, Inc., New York, N. Y., 1964, p 323; (e) E. M. Kosower, "Introduction to Physical Organic Chemistry, John Wiley & Sons, Inc., New York, N. Y., 1968, p 45; (f) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 171 ff; (g) P. R. Wells, "Linear Free Energy Relationships," Academic Press, London, 1968.

Table II. Analytical and Spectral Data for Adducts from 1,1-Diarylethylenes ($(p\text{-}XC_6H_4)_2C{=}CH_2$) and Diphenylketene

Formula	Microanalysis						Mp,[a]	Infrared,	Nmr, τ,
	Calcd, %			Found, %					
(X)	C	H	Cl	C	H	Cl	°C	cm^{-1}	ppm[b]
$C_{42}H_{32}O_2$ (H)	88.70	5.67		88.41	5.61		182	1745 1490	2.5–3.4 (m) 5.10 (s) 6.55 (s)
$C_{44}H_{36}O_2$ (CH_3)	88.56	6.08		88.53	5.89		103	1743 1510 1493	2.8–3.4 (m) 5.15 (s) 6.55 (s) 7.65 (s)
$C_{42}H_{30}O_2Cl_2$ (Cl)	79.12	4.74	11.12	79.26	4.87	10.98	8160	1743 1492	2.6–3.4 (m) 5.10 (s) 6.55 (s)
$C_{44}H_{36}O_4$ (OCH_3)	84.05	5.77		83.56[c]	5.80		162	1740 1603 1509 1250	2.7–3.4 (m) 5.15 (s) 6.15 (s) 6.58 (s)
$C_{44}H_{30}O_2F_6$ (CF_3)	74.99	4.29		75.30	4.31		22	1734 1498 1330 1162 1134	2.4–3.2 (m) 5.05 (s) 6.4 (s)

[a] From ethanol or petroleum ether. [b] For integration data, see text. [c] Incomplete combustion led to low values for carbon in a number of determinations.

of the rate constants *vs.* 2σ, twice the Hammett substituent constant.[10] A fairly good linear free energy is obtained, with the point for the *p*-chloro-substituted olefin being responsible for the greatest deviation from linearity. The ρ value, a measure of the sensitivity of the reaction rate to substituent changes, is −0.74 ± 0.13 if the chloro-substituted olefin is included and −0.78 ± 0.01 if it is not, both values being obtained from the least-squares plot of the rate constants *vs.* 2σ.

Analytical and spectral data for the adducts isolated after several kinetic runs or from parallel larger scale reactions are summarized in Table II. The nmr spectra of the adducts, typically exhibiting two singlets at about τ 5.1 and 6.5 in a 1:2 ratio in addition to the expected aromatic, methyl, and methoxyl proton absorptions, rule out structural proposals **1** and **2** for these compounds. The structure of these adducts and the kinetics of the reaction of 2,2,3,3-tetraphenylcyclobutanone with diphenylketene are under continuing investigation.

Diphenylketene and styrene give the cycloadduct 2,2,3-triphenylcyclobutanone in nearly quantitative yield when heated above room temperature, and several analogs prepared from the addition of diphenylketene to substituted styrenes have also been reported.[4,11,12]

Kinetic studies of the diphenylketene–styrene addition were carried out in a manner entirely analogous to those of the diphenylketene–1,1-diarylethylene system. During analyses, the nmr probe was cooled to −5° (±5°). Within the accuracy of integration, there was no change in the spectrum of a reaction mixture at this temperature over periods of up to 2 hr. The reaction was followed by observing the disappearance of the styrene methylene protons relative to an internal standard, hexamethylbenzene or *p*-di-*t*-butylbenzene. The data were analyzed as before.

p-Trifluoromethylstyrene was prepared by the reaction of *p*-trifluoromethylphenylmagnesium bromide with acetaldehyde, and dehydration of the resulting alcohol with phosphorus pentoxide. *p*-Methoxystyrene was prepared by the lithium aluminum hydride reduction of *p*-methoxyacetophenone or by the treatment of *p*-methoxybenzaldehyde with methylmagnesium iodide, followed by dehydration of the intermediate 1-(*p*-methoxyphenyl)ethanol. The other styrenes were obtained from commercial sources.

Under the reaction conditions employed, *p*-methoxystyrene underwent rapid polymerization. The reaction of *p*-nitrostyrene with diphenylketene began slowly, then increased rapidly in rate with consumption of diphenylketene to give a viscous gel. Filtration of the reaction mixture gave a white powder, insoluble in acetone or chlorinated hydrocarbons and exhibiting a strong band at about 2280 cm^{-1} in the infrared. Neither *p*-methoxy- nor *p*-nitro-substituted styrene was included in the kinetic study.

The results for other kinetic runs are given in Table III. The reaction is first order in ketene and first order in olefin as would be expected from the stoichiometry. A Hammett linear free energy treatment of the data (Figure 3) gives a ρ value of −0.67 (±0.25) using σ constants. The point for the *p*-chloro olefin, as in the diarylethylene series, is significantly removed from the best straight line through the remaining points. If it is excluded from the calculations, a ρ value of −0.73 (±0.003) is obtained.

Table III. Rate Constants for the Addition of Diphenylketene to Substituted Styrenes in Bromobenzene at 119.96°

X ($p\text{-}XC_6H_4CH{=}CH_2$)	σ	$k \times 10^2$, l./mol min
CF_3	+0.54	1.71 ± 0.17
Cl	0.23	4.69 ± 0.16
H	0	4.20 ± 0.19
CH_3	−0.17	5.66 ± 0.47

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(10) The values of σ were taken from the compilation by J. S. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 87.

(11) H. Staudinger and A. Rheiner, *Helv. Chim. Acta*, 7, 8 (1924).

(12) E. Bergmann and O. Blum-Bergmann, *J. Chem. Soc.*, 727 (1938).

A determination of the relationship between solvent polarity and rate[13] of cycloaddition between diphenylketene and styrene was made with the solvents bromobenzene (ϵ = 5.4), *o*-dichlorobenzene (ϵ = 9.9), di(β-chloroethyl) ether (ϵ = 21.2), and dimethylformamide (ϵ = 38).[14] In dimethylformamide, and to a lesser extent in di(β-chloroethyl)ether, the reaction rates began to differ from good second-order kinetics, exhibiting a rate decrease, at about 60–70% reaction. Because of the low volatility of DMF it was difficult to isolate quantitatively products from the reaction mixture; nevertheless, 85–90% of the normal diphenylketene–styrene adduct could be obtained.

The results of the solvent effect studies and available E_T values[15] are shown in Table IV. There is a slight rate decrease with increasing dielectric constant of the solvent, just barely outside of experimental error.

Table IV. Rate Constants for the Addition of Diphenylketene to Styrene at 119.96° in Solvents of Varying Dielectric Constant

Solvent	ϵ^a	$E_T{}^b$	$k^c \times 10^2$, l./mol min
Bromobenzene	5.4	37.5	4.20
o-Dichlorobenzene	9.9		4.00
Di(β-chloroethyl) ether	21.2		3.90^d
Dimethylformamide	38	43.8	3.62^d

[a] From ref 14. [b] See ref 15. [c] Average esd = 0.25. [d] To approximately 55% reaction where deviation from second-order kinetics became significant.

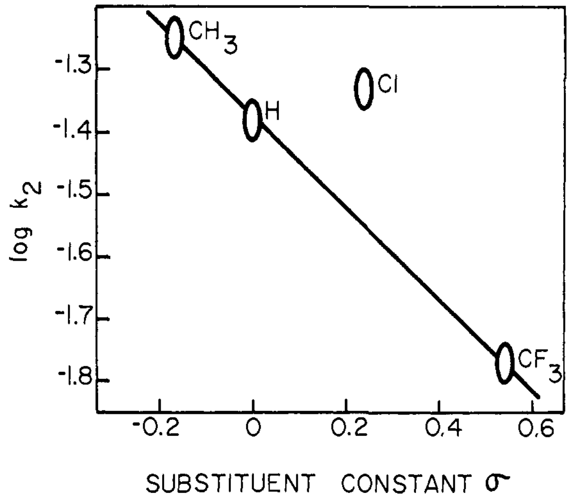

Figure 3. Plot of log k_2 against σ for the reaction of diphenylketene with 4-substituted styrenes 119.96° in bromobenzene.

Analysis and Conclusions

The sign of ρ for the reactions of both 1,1-diarylethylenes and styrenes indicates that in the transition states positive charge develops to some extent in the olefinic portion of the molecule. This is, of course, what would be expected from the observed orientation of ketene–olefin cycloadditions on the basis of a mechanism involving a dipolar intermediate, a diradical with some dipolar character,[16,17] or a concerted mechanism with some sensitivity to polar effects in the transition state.

The magnitude of ρ obtained from both Hammett plots (−0.78, −0.73) is quite different from those observed for typical ionic processes (−3.3 to −4.3).[18] The contrast might well be even larger if comparable solvents could have been employed. Most ρ values tend to increase with decreasing dielectric constant of the reaction medium;[13c] while all of the polar reactions cited[18] were carried out in solvents of high dielectric constant (alcohols, acids, aqueous acetone), the current study empoyed bromobenzene, a solvent of low dielectric constant (ϵ = 5.4) which most likely inflates the observed ρ value.

Radical and NBS bromination of substituted toluenes,[19] and the radical decomposition of *t*-butyl phenylperacetates,[20] show smaller negative ρ values (−1.4 to −1.0).

The Diels–Alder reaction of 1-aryl-1,3-butadienes with maleic anhydride gives a ρ of −0.62 at 45°.[21]

Through comparison of the ρ values observed in the present work with precedent one might conclude that a concerted reaction, similar to the Diels–Alder prototype, or possibly a diradical process is indicated. The absolute rates for the two cycloadditions investigated, however, seem quite incompatible with a mechanistic formulation postulating generation of a radical center at the carbon adjacent to the substituted phenyl groups in the rate-determining transition states. The progression from one phenyl to two phenyls increases the rates of radical reactions at the adjoining carbon: for instance, the relative reactivity per hydrogen toward bromine atoms for toluene and diphenylmethane is 1:9.4,[22] and the relative rates for addition of methyl radicals to styrene and 1,1-diphenylethylene are 1:1.9.[23] In the cycloadditions with diphenylketene, the relative rates for styrene and 1,1-diphenylethylene are in a 62:1 ratio. The only apparent prospect for sustaining the radical formulation, hypothesizing severe steric interactions in the transition state to account for the slower rate with 1,1-diphenylketene, cannot be sustained: with the steric interactions would unavoidably come electronic interactions making a diradical model developed in detail indistinguishable conceptually or operationally from a concerted mechanism.

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(13) For reviews see (a) ref 9e, p 259; (b) ref 9f, p 263; and (c) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964.

(14) A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Toops, Jr., "Organic Solvents," Technique of Organic Chemistry, Vol. VII, 2nd ed, A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1955.

(15) K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. Chem.*, **661**, 1 (1963).

(16) F. R. Mayo and C. Walling, *Chem. Rev.*, **46**, 191 (1950).

(17) G. A. Russell, *J. Org. Chem.*, **23**, 1407 (1958).

(18) (a) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958); (b) K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1964, p 404; (c) W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964); (d) J.-P. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 52 (1966); (e) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964); (f) J. E. Dubois and W. V. Wright, *ibid.*, 3101 (1967); (g) E. D. Bergmann, J. E. Dubois, and A. F. Hegarty, *Chem. Commun.*, 1616 (1968); (h) S. Nishida, *J. Org. Chem.*, **32**, 2692, 2697 (1967); (i) E. Berliner and M. Q. Malter, *ibid.*, **33**, 2595 (1968).

(19) R. E. Pearson and J. C. Martin, *J. Amer. Chem. Soc.*, **85**, 354 (1963).

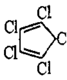
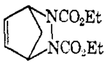
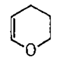
(20) P. D. Bartlett and C. Rüchardt, *ibid.*, **82**, 1756 (1960).

(21) E. J. DeWitt, C. T. Lester, and G. A. Ropp, *ibid,*, **78**, 2101 (1956); see also I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958), and D. N. Matthews and E. I. Becker, *ibid.*, **31**, 1135 (1966).

(22) G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963).

(23) M. Szwarc and J. H. Binks in "Theoretical Organic Chemistry," Kekulé Symposium, 1958, Butterworth Scientific Publications, London, 1958.

Table V. Solvent Effects on the Rates of Selected Cycloadditions

Addends	$\Delta\epsilon$[a]	ΔE_T[b]	Δrate[c]	Ref
1. $(H_5C_6)_2C{=}C{=}O + H_5C_6CH{=}CH_2$	5–38	37–44	−1.2	
2. $(NC)_2C{=}C(CN)_2 + p\text{-}CH_3OC_6H_4CH{=}CH_2$	2–59		5×10^4	*d*
3.  + $H_5C_6CH{=}CH_2$	2–38	34–44	1.7	*e*
4. $(H_5C_6)_2C{=}N_2$ + 	2–38	34–44	1.2	
5. $(H_5C_6)_2C{=}C{=}O$ + 	2–38	34–44	−3.6	*g*
	2–36	34–46	50	*h*
6. $(H_5C_6)_2C{=}C{=}O + n\text{-}C_4H_9OCH{=}CH_2$	2–36	34–46	160	*h*
7. $(H_3C)_2C{=}C{=}O + (H_3C)_2C{=}C{=}O$	2–36	34–46	29	*i*

[a] Solvent range in dielectric constant; values from ref 14. [b] Solvent range in E_T; *cf.* ref 15. [c] Ratio of the largest to smallest rate constant observed over the noted solvent dielectric constant range; a negative Δrate indicates a decrease in rate with increasing dielectric constant. [d] J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, **84**, 2210 (1962). [e] J. Sauer, *Angew. Chem. Intern. Ed. Engl.*, **6**, 16 (1967). [f] R. Huisgen, *Angew. Chem.*, **75**, 742 (1963). [g] W. T. Brady and H. R. O'Neal, *J. Org. Chem.*, **32**, 612 (1967). [h] R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Lett.*, 4485 (1968). [i] R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, **90**, 5342 (1968).

We conclude, then, from the magnitude of the ρ values observed and the relative rates of the two sets of reactants, that the cycloaddition of diphenylketene with styrenes is a concerted process, and the rate-determining step in Scheme Ia leading toward the 2:1 adduct is the concerted formation of a 2,2-diphenyl-3,3-diarylcyclobutanone rather than the dipolar intermediate **3**.

The small solvent effects on the diphenylketene–styrene addition are similar to those observed for Diels–Alder reactions and for several (2 + 3) cycloadditions (Table V). Again the additions studied here may be classed as concerted. Further examples of solvent effects on the rates of various types of cycloadditions have been gathered in Table I of Gompper's review.[6]

The stereospecificity and the secondary deuterium kinetic isotope effects of the diphenylketene–styrene reaction[24] also support the conclusion that the cycloaddition is concerted.

Experimental Section

Melting points were obtained on a Kofler micro heating stage using a calibrated thermometer; boiling points are uncorrected. Infrared spectra were taken on Perkin-Elmer Models 21, 137, and 521 spectrophotometers. Nmr spectra were recorded on Varian Associates Model A-60, A-60A, A-56/60, or HA-100 spectrometers; many were obtained by Messrs. R. Thrift, L. Brodsky, and their associates. Gas–liquid partition chromatographic separations were carried out using Varian Aerograph A90-P, A90-P3, and 1520 model instruments equipped with a Brown or Leeds and Northrup recorder and Disc integrator. Microanalyses were carried out by Mr. J. Nemeth and his associates, Urbana, Ill.

Diphenylketene was prepared from benzil monohydrazone through oxidation with mercuric oxide and thermal decomposition of the resultant phenylbenzoyldiazomethane,[25] or, more conveniently, through dehydrohalogenation of diphenylacetyl chloride[26] with dry triethylamine in benzene.[27] Diphenylketene was stored at 7° under nitrogen and freshly redistilled at reduced pressure under a nitrogen atmosphere just prior to use.

1,1-Diarylethylenes. The 1,1-diarylethylenes studied, with the exception of 1,1-bis(*p*-trifluoromethylphenyl)ethylene and 1,1-diphenylethylene (Eastman), were prepared by the reaction of methylmagnesium iodide with the corresponding *para,para'*-disubstituted benzophenone followed by dehydration of the diarylmethylcarbinol.[28] Melting points and yields are given in Table VI.

Table VI. 1,1-Diarylethylenes

$(p\text{-}XC_6H_4)_2\text{-}C{=}CH_2$, X	Yield, %[a]	Mp, °C	Lit. mp, °C
$(CH_3)_2N$	89	125–126	121–122[c]
CH_3O	65	141–142	142–143
CH_3	76	59–60	61[c]
Cl	79[b]	84–86	84–86[d]
CF_3	48	33–34	

[a] Based on the starting benzophenone. [b] Based on the intermediate 1,1-bis(*p*-chlorophenyl)ethanol. [c] Reference 28a. [d] Reference 28b.

***para*-Substituted Styrenes.** With the exception of *p*-trifluoromethylstyrene, the substituted styrenes used in this work were commercially available. Styrene, *p*-chlorostyrene, and *p*-methylstyrene (Aldrich) were distilled prior to use. The refractive indices agreed with the published values,[29] and the nmr spectra were as expected. *p*-Nitrostyrene (Borden Monomer–Polymer Laboratories) as received contained *p*-nitrophenylethane and an unidentified impurity absorbing at τ 4.6 (s) in the nmr. As *p*-nitrostyrene decomposes on distillation, the material was purified by four recrystallizations from petroleum ether in a 0° cold room.[30]

***p*-Trifluoromethylstyrene.** To the Grignard reagent derived from 0.111 mol each of *p*-trifluoromethylbromobenzene and magnesium turnings in 70 ml of ether was added 4.9 g (0.111 mol) of freshly distilled acetaldehyde in 100 ml of benzene at a rate causing the ether to reflux. The mixture was stirred at room temperature overnight and decomposed by the addition of dilute sulfuric acid. The ethereal layer was separated, washed wih aqueous sodium bicarbonate and water, dried over magnesium sulfate, and filtered, and ether was removed from the filtrate under vacuum to leave the crude alcohol. The alcohol was dehydrated by dissolving it in 100 ml of benzene and heating a mixture of this solution and 15 g

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of phosphorus pentoxide for 5 hr at reflux. The benzene solution was decanted and distilled to give olefin and unreacted alcohol. A second distillation gave 5.4 g (52% yield allowing for recovered alcohol) of *p*-trifluoromethylstyrene, bp 66–68° (40 mm) [lit.[31] bp 65.8° (40 mm)], $n^{25}\text{D}$ 1.4650 (lit.[31] $n^{25}\text{D}$ 1.4648). The nmr spectrum contained absorptions at τ 2.6–3.1 (m, 4 H), 3.2–3.7 (m, 1 H), and 4.2–5.0 ppm (m, 2 H). Analysis by glpc showed one principal component with a small amount (<0.4%) of a compound identified as the *p*-*t*-butylphenol added as a polymerization inhibitor during the distillation. Attempts to dehydrate 1-(*p*-trifluoromethylphenyl)ethanol by distillation from powdered potassium hydroxide and at reflux with 25% sulfuric acid were unsuccessful. The recovered alcohol was used for the successful dehydration described above, and losses incurred in recovery may partially account for the low overall yield of olefin.

1,1-Bis(*p*-trifluoromethylphenyl)ethylene. A reaction mixture containing the Grignard reagent from 0.111 mol each of magnesium turnings and *p*-trifluoromethylbromobenzene was cooled in ice water and a solution of 4.1 g (0.047 mol) of ethyl acetate in 5 ml of ether was added over a period of 10 min. The reaction was stirred for 15 min at room temperature, then returned to the ice bath, and a solution of 5 g of ammonium chloride in 20 ml of water was added dropwise. A dense precipitate formed, and the mixture was allowed to stand for 30 min.

The ethereal phase was separated, and the solid materials were extracted with two 25-ml portions of ether. The combined organic layers were dried over calcium sulfate, filtered, and concentrated under vacuum to leave a dark red oil. The crude alcohol was heated to 210° for 20 min, allowed to cool, and combined with 15 ml of 20% sulfuric acid. The mixture was heated at reflux for 1 hr and cooled to room temperature. The organic materials were taken up in ether, washed, dried over calcium sulfate, filtered, and concentrated. The remaining oil was dissolved in a minimum of hot ethanol. On cooling a tan precipitate formed which on standing, however, turned dark brown. Distillation removed the ethanol, gave a fraction of bp 55–70° (0.5 mm) containing *p*-trifluoromethylacetophenone (bands at 1685, 1320, and 1200–1100 cm^{-1} in the infrared), and provided the crude olefin, bp 85–110° (0.8 mm), 8.5 g (48%). Two vacuum distillations gave material boiling at 81–82° (0.35 mm) which showed only one peak on glpc analysis (20% SE-30 on Chromosorb W, 1.7 m, 100°). The melting point (uncorrected) was 33–34°. The nmr spectrum of the olefin exhibited absorptions at τ 2.25–2.75 (m, 8 H) and 4.4 ppm (s, 2 H). The infrared spectrum showed strong absorptions at 1630, 1320, 1100–1200, and 920 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}F_6$: C, 60.77; H, 3.18. Found: C, 60.87; H, 3.44.

Kinetics of the Reaction of 1,1-Diarylethylenes with Diphenylketene. Diphenylketene was vacuum distilled under a nitrogen atmosphere just prior to use. The 1,1-diarylethylenes were purified by distillation or recrystallization until the samples had correct analyses for carbon and hydrogen and, in the case of liquid samples, appeared to contain a single component by glpc. Bromobenzene (reagent) was dried over calcium sulfate and distilled prior to use. The two nmr standards, hexamethylbenzene and *p*-di-*t*-butylbenzene, were recrystallized to constant melting point.

Standard nmr tubes were specially prepared by joining an 8- to 10-cm length of similar diameter tubing to the open end and constricting slightly at this juncture. The tubes were base washed, water washed, and dried in an oven. The samples were weighed out into volumetric flasks which had been washed, dried, and flushed with nitrogen, and 1-ml aliquots were transferred by syringe to the nitrogen-flushed nmr tubes. The tubes were attached to a high vacuum line using an adaptor fitted with a ground-glass socket joint at the end attached to the vacuum line, a high vacuum stopcock, and an Ace Glass "O"-ring screw seal at the end attached to the modified nmr tube. The tubes were cooled in liquid nitrogen, evacuated, and sealed with the stopcock. The liquid nitrogen was removed slowly. After the degassing process was complete, the tubes were again cooled in liquid nitrogen and the stopcock was opened to evacuate the tube. This process was repeated until the vacuum gauge of the system showed no pressure increase on opening the stopcock. The tube was then sealed off at the constriction with a hand torch.

The time zero nmr spectrum was taken with multiple integrations of the olefin and standard absorptions. This ratio was used to relate the olefin:standard ratio at later times to the olefin concentration. The tubes were placed in a silicone oil kinetic bath at 119.96 ± 0.02° for timed intervals, removed, and quenched in an ice–water bath; multiple integration of the olefin and standard absorptions was accomplished using the electronic integrator of a Varian nmr instrument.

The reaction was found to be negligibly slow at ambient nmr probe temperatures; after 2 hr at probe temperature there was no detectable change of the spectrum. There was apparently little or no vapor phase reaction or concentration change due to volatile components vaporizing into the unfilled portion of the tube; tubes filled to different heights led to no differences in the nmr integrals as a function of time.

Adducts from reactions of 1,1-diarylethylenes with diphenylketene in bromobenzene were isolated from sealed tube reactions or recovered from nmr samples used in the kinetic study. Recrystallization from ethanol or benzene–petroleum ether (1,1-diphenylethylene adduct) gave the analytically pure products (Table II).

Kinetics of the Reaction of *para*-Substituted Styrenes with Diphenylketene. The procedures used in the 1,1-diarylethylene–diphenylketene kinetic study were employed, with appropriate modifications. *o*-Dichlorobenzene (Eastman, 99+% grade) was dried over phosphorus pentoxide and distilled, $n^{20}\text{D}$ 1.5512 (lit.[14] $n^{20}\text{D}$ 1.5514). N,N-Dimethylformamide was dried over calcium hydride and distilled from calcium hydride; $n^{25}\text{D}$ 1.4269 (lit.[14] $n^{25}\text{D}$ 1.4269). Di(β-chloroethyl) ether (Eastman) was dried over calcium sulfate and distilled; $n^{20}\text{D}$ 1.4570 (lit.[14] $n^{20}\text{D}$ 1.4575).

Because the reaction between the styrenes and diphenylketene is not negligibly slow at nmr probe temperatures, the probe was cooled to −5° (±5°) using a Varian Associates Model V-6040 variable-temperature control with a thermocouple bridge for temperature measurement. Within the limits of experimental error, there was no change in the spectrum of a sample kept at this temperature for periods up to 2 hr. Disappearance of the styrene methylene absorptions was followed relative to an internal standard, hexamethylbenzene or *p*-di-*t*-butylbenzene.

2,2-Diphenyl-3-arylcyclobutanones. The 2,2-diphenyl-3-arylcyclobutanones prepared from diphenylketene and *p*-methylstyrene, *p*-chlorostyrene, and *p*-methoxystyrene have been described in the literature and were prepared in a manner entirely analogous to that employed for the preparation of 2,2,3-triphenylcyclobutanone.[4] The adduct 2,2-diphenyl-3-(*p*-trifluoromethylphenyl)cyclobutanone was prepared by heating equimolar amounts of diphenylketene and *p*-trifluoromethylstyrene in a sealed tube under nitrogen at 80° for 72 hr. The proton nmr spectrum had absorptions at τ 2.3–3.3, 5.4 (t, 1 H), and 6.55 (d, 2 H). Recrystallization from petroleum ether gave white crystals, mp 75–76°.

Anal. Calcd for $C_{23}H_{17}F_3O$: C, 75.40; H, 4.68. Found: C, 75.15; H, 4.72.

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